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METHOD AND COMPOSITION FOR INHIBITING SILVER SLUDGE IN THIOSULFATE MONOBATHS

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This invention relates to photography and, more particularly, to a method and composition for preventing and/or inhibiting the formation of silver sludge during photographic processing employing a monobath containing a thiosulfate fixing agent.

Monobaths containing a water-soluble thiosulfate, such as sodium thiosulfate, as the fixing agent has been known for a number of years. Monobath compositions offer inviting possibilities for processing an exposed photographic silver halide emulsion to produce a silver image because development and fixation or stabilization (of unexposed silver halide) can be accomplished in one simple operation.

However, one of the major disadvantages accompanying the use of such monobath compositions is the formation and deposition of silver sludge when the monobath composition is employed to process photographic silver halide materials in a continuous manner. See H. A. Miller and J. I. Crabtree—"Amer. Phot.," vol. 42 (1948), page 76 and W. M. Drumm—"Phot. Sci. and Eng.," vol. 1 (1958), page 147. If the monobath is warmed slightly to increase the rate of processing, this has the further disadvantage of accelerating the deposition of the undesirable silver sludge. More often than not, these silver deposits cling to equipment as well as processed materials, and are difficult to remove.

Attempts have been previously made to control silver sludging in monobaths by a variety of techniques, one method being to employ coagulants to cause the silver sludge to settle to the bottom of the processing solution. Another technique is to use active nuclei, or silver precipitating agents, such as Carey-Lea silver. While these methods do have some effect upon the degree of sludging, they are not able to substantially eliminate the sludge, or to inhibit the formation of such sludge for a period of time sufficiently long to make continuous processing possible.

We have now found that the problem of silver sludging in thiosulfate monobaths can be substantially eliminated or controlled by using certain mercapto compounds in the monobath composition.

It is, therefore, an object of our invention to provide a method of controlling the formation and deposition of silver sludge in monobath compositions for processing silver halide photographic materials. Another object is to provide a method of continuous processing of large amounts of photographic silver halide materials over extended periods of time without the disadvantages accompanying the formation of silver sludge. Still another object is to provide novel compositions of matter useful in monobath processing. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, photographic silver halide materials which have been exposed in the normal manner are subjected to monobath processing employing alkaline aqueous developing solutions containing one or more photographic developers capable of reducing exposed silver halide to metallic silver, a water-soluble thiosulfate, in sufficient quantity to stabilize or remove substantially all unexposed silver halide, and a water-soluble heterocyclic mercapto compound. A number of heterocyclic compounds have been previously employed in photographic emulsions or developing compositions for the purpose of controlling image tone. However, we have found that the mercapto compounds useful in our invention are unique in controlling or preventing the formation of silver sludge during monobath processing. Heterocyclic mercapto compounds closely related to those used in our invention frequently have little or no useful activity in preventing the formation of silver sludge during monobath processing. For example, 2-mercapto-5-o-hydroxyphenyl-1,3,4-thiadiazole is especially useful in our invention in preventing the formation of silver sludge, while the isomeric para hydroxy compound has little or no observable effect in preventing or controlling the formation of silver sludge.

Particularly useful heterocyclic mercapto compounds of our invention comprise 1-phenyl-5-mercaptotetrazole, 2-mercapto-5-o-hydroxyphenyl-1,3,4-thiadiazole, 2-mercapto-5-o-tolyl-1,3,4-oxadiazole, 2-mercapto-5-phenyl-1,3,4-oxadiazole, 2-mercapto-5-p-nitrophenyl-1,3,4-oxadiazole, 2-mercapto-5-cyclohexyl-1,3,4-thiadiazole, 2-mercapto-5-m-nitrophenyl-1,3,4-oxadiazole, etc. Another useful heterocyclic compound for processing certain photographic silver halide emulsions is 2-benzoxazolethiol. This benzoxazole compound is useful in processing high speed negative photographic silver bromiodide emulsions. The monobath compositions of our invention are generally quite useful in processing a variety of photographic silver halide materials where the silver halide can be, for example, silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide, etc.

The monobath compositions of our invention can comprise any of the conventional water-soluble thiosulfate fixing agents, such as the alkali metal, e.g., sodium, potassium, etc., thiosulfates, ammonium thiosulfate, etc. The concentration of the thiosulfate compound can be varied, but it is important to have the concentration sufficiently high to fix or stabilize substantially all of the unexposed silver halide. For the purposes of our invention, we have found that the thiosulfate concentration should be at least about 80 grams per liter. The maximum concentration of thiosulfate is primarily a function of the concentration of the silver halide in the emulsion being processed. Frequently, concentrations as high as 160 grams of thiosulfate per liter of monobath composition can be employed and good quality prints can be produced in 5 seconds or less using such compositions. Of course, if the concentration of silver halide in the emulsion is increased, then it is possible that amounts of thiosulfate in excess of 160 grams per liter can be employed.

The concentration of heterocyclic mercaptan used in our invention can be varied, but we have found that especially useful results can be obtained where the concentration varies from about 0.001 gram per liter to about 1.0 gram per liter, with especially useful results being obtained within the range of about 0.1 to about 0.5 gram per liter. The heterocyclic mercaptan need not be employed in the form of the free mercaptan, but can be used in the form of a water-soluble salt, such as sodium, potassium, etc.

The pH of the monobath compositions of our invention can be varied, but especially useful results have been obtained at pH's of at least about 10 to pH's as high as about 12 or 12.5.

Any of the ordinarily employed silver halide developing agents for rapidly producing a silver image can be employed in our invention. Especially useful results have been obtained using the well known 3-pyrazolidone developing agents. A number of such developing agents are described in the copending application, Serial No. 134,014, filed August 5, 1961, now abandoned, of P. H. Steward, G. E. Fallesen and J. W. Reeves, Jr. Typical of pyrazolidone developing agents useful in the monobath compositions of our invention include 1-phenyl - 3 - pyrazolidone, 1 - phenyl - 4,4 - dimethyl - 3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-phenyl - 4 - methyl - 3 - pyrazolidone, 1,5 - diphenyl - 3-pyrazolidone, 1-p-tolyl-3-pyrazolidone, 1-phenyl-2-acetyl-4,4-dimethyl-3-pyrazolidone (acetyl group hydrolyses off to yield active developing agent), 1-p-hydroxyphenyl-4,4 - dimethyl - 3 - pyrazolidone, 1 - (2 - benzothiazolyl) - 3 - pyrazolidone, 3 - acetoxy - 1 - phenyl - 3-pyrazolidone (acetoxy group hydrolyses off to yield active developer), etc. These 3-pyrazolidone developing agents are particularly useful and they can be incorporated partly or wholly within the photographic element undergoing development. However, for rapid monobath processing, it is desirable to generally have sufficient pyrazolidone developing agent in the aqueous developing solution to effect rapid processing. Other black-and-white photographic developing agents which can be employed alone or in combination with the 3-pyrazolidone include hydroquinone, N-methyl-p-aminophenyl sulfate, chlorohydroquinone, etc. The concentration of the developing agent in the monobath composition can be varied, depending upon the particular photographic material undergoing development. As indicated above, the 3-pyrazolidone developing agents are particularly useful, since they can be incorporated directly into the photographic material either in a layer contiguous to the emulsion layer or in the emulsion layer itself (particularly where a development precursor is used, such as 3-acetoxy-1-phenyl-3-pyrazolidone).

The following examples will serve to illustrate briefly the operation of our invention.

Example 1

The following photographic monobath composition was prepared:

	Grams
4-methyl-1-phenyl-3-pyrazolidone	4.0
Hydroquinone	12.0
Sodium sulfite, desiccated	70.0
Sodium hydroxide	3.0
Sodium metaborate, octahydrate	40.0
Sodium thiosulfate, crystalline	100.0
Water to make	10.2

pH=10.2.

One liter of the above monobath was used to process 20 sheets, 8½ x 11 inches, of exposed silver chloride document copying photographic papers for a period of 10 seconds at room temperature. upon standing for one hour, the used monobath solution produced a heavy gray to black precipitate which deposited upon the vessel used for development. The prints produced by this development had high image density, low fog, and excellent stability to strong actinic light.

A second monobath composition identical to the above composition was prepared, except that 0.2 gram per liter of 1-phenyl-5-mercaptotetrazole was added. When 20 prints of identical photographic paper were processed under the same conditions described above, no silver sludge appeared for a period longer than 24 hours. After a period of one week, only a very slight accumulation of black particles could be seen. The prints had image density, fog and stability characteristics equal or superior to those processed in the monobath containing no mercaptotetrazole compound.

Example 2

Photographic papers comprising an ordinary photographic silver chloride emulsion were processed in a monobath composition similar to that described in Example 1 above, except that it contained 0.2 gram per liter of 2-mercapto-5-o-hydroxyphenyl-1,3,4-thiadiazole instead of the tetrazole compound. After 20 prints had been processed through this monobath composition and the composition allowed to stand for 24 hours, the monobath composition remained sludge-free.

Example 3

The 1-phenyl-5-mercaptotetrazole of Example 1 was replaced with 0.2 gram per liter of 2-mercapto-5-o-tolyl-1,3,4-oxadiazole. After processing 20 photographic paper sheets comprising an ordinary photographic silver chloride emulsion in this monobath and allowing it to stand for 24 hours, no sludge could be detected.

Example 4

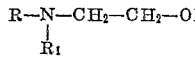
The phenyl mercaptotetrazole of Example 1 was replaced with 0.2 gram per liter of 2-mercapto-5-phenyl-1,3,4-oxadiazole. Again, the monobath composition remained sludge-free at least 24 hours after processing 20 photographic prints.

In a manner described in the above examples, other tetrazole, thiadiazole and oxadiazole compounds of this type described above can be employed to prevent silver sludging in monobath compositions comprising both developing agent and fixing or stabilizing agent. While the mechanism of our invention is not fully understood, it is believed that it is concerned with rendering silver and/or silver sulfide nuclei, produced on development and fixation, incapable of catalyzing the reduction of the silver thiosulfate complex by strong adsorption of the heterocyclic mercaptan to the nuclei. If the adsorbed nuclei are soluble, no sludging occurs, but if these adsorbed nuclei are not sufficiently soluble in the monobath, a white or near white precipitate is immediately formed.

One commercially available monobath preparation currently available contains sodium thiosulfate, and it is recommended to use room temperature processing for 5 to 8 minutes. It is stated that a print capacity of 8000 square inches of paper per gallon of monobath is possible using this composition. In commercial processing, it has frequently been found that useful capacity of separate developers and fixers seldom exceeds 10,000 square inches per gallon of either developer or fixer. Contrasted with the foregoing, we have found that the useful tray capacity of the monobath compositions of our invention is extended to 70,000 square inches of paper per gallon for a period exceeding two weeks. This increased processing capacity is realized without deleterious changes in photographic quality during this period. The normal reduction in developing activity due to aerial oxidation and exhaustion is counterbalanced in our system by withholding a part of the thiosulfate content in the form of silver thiosulfate complex. When the complex is eventually destroyed, re-entry of the thiosulfate causes severe degradation of the developed image. This effect does not occur when processed with our novel monobath compositions.

It has also been found that the developing rate of our novel monobaths can be accelerated by adding a small quantity of a water-soluble hydroxyalkylamine compound. Moreover, such hydroxyalkylamine compounds frequently give improved solution life and greater image stability. Typical hydroxyalkylamine compounds useful in our invention include ethanolamine, 2,2'-iminodiethanol, 2,2',2''-nitrilotriethanol (triethanolamine), N-mono-

methylethanolamine, N-monoethylethanolamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, etc. Particularly useful hydroxyalkylamines include those represented by the following general formula:



wherein R and R_1 each represents a hydrogen atom, a lower alkyl radical (e.g., methyl, ethyl, propyl, etc.), or a hydroxyalkyl radical (e.g., β-hydroxyethyl, β-hydroxypropyl, etc.).

A particularly useful monobath composition was prepared according to the method described in Example 1 above by including about 9 grams of ethanolamine in the composition. The combination of the mercaptotetrazole compound and the ethanolamine compound gave particularly useful results, insofar as freedom from sludge and development speed were concerned. Excellent photographic quality was obtained using such combinations. The amount of hydroxyalkyl compound used can be varied. We have found that from about 5 to 20 grams per liter give quite useful effects.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, a water-soluble hydroxyalkylamine, and from about 0.001 to about 1.0 gram per liter of solution of a heterocyclic mercaptan capable of adsorbing silver compounds formed by photographic development to solubilize such silver compounds, said heterocyclic mercaptan being selected from the class consisting of mercaptotetrazoles, mercapto-1,3,4-oxadiazoles and mercapto-1,3,4-thiadiazoles.

2. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of a water-soluble heterocyclic mercaptan which renders silver containing precipitating nuclei soluble upon adsorption of said mercaptan thereto, said heterocyclic mercaptan being selected from the class consisting of mercaptotetrazoles, mercapto-1,3,4-oxadiazoles and mercapto-1,3,4-thiadiazoles.

3. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 1-phenyl-5-mercaptotetrazole.

4. A monobath composition according to claim 3 wherein said silver halide developing agent is a 3-pyrazolidone.

5. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-o-hydroxyphenyl-1,3,4-thiadiazole.

6. A monobath composition as defined in claim 5 wherein said silver halide developing agent is a 3-pyrazolidone.

7. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-o-tolyl-1,3,4-oxadiazole.

8. A monobath composition as defined in claim 7 wherein said silver halide developing agent is a 3-pyrazolidone.

9. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-phenyl-1,3,4-oxadiazole.

10. A monobath composition as defined in claim 9 wherein said silver halide developing agent is a 3-pyrazolidone.

11. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-p-nitrophenyl-1,3,4-oxadiazole.

12. A monobath composition as defined in claim 11 wherein said silver halide developing agent is a 3-pyrazolidone.

13. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-cyclohexyl-1,3,4-thiadiazole.

14. A monobath composition as defined in claim 13 wherein said silver halide developing agent is a 3-pyrazolidone.

15. A monobath composition for simultaneously developing and fixing an exposed photographic silver halide emulsion layer comprising an aqueous alkaline solution of a photographic silver halide developing agent for reducing exposed silver halide to metallic silver, at least 80 grams per liter of solution of a water-soluble thiosulfate, and from about 0.001 to about 1.0 gram per liter of 2-mercapto-5-m-nitrophenyl-1,3,4-oxadiazole.

16. A monobath composition as defined in claim 15 wherein said silver halide developing agent is a 3-pyrazolidone.

17. In a method of processing in a continuous fashion large quantities of exposed photographic silver halide emulsion layers coated on a paper support by developing said emulsion layers in a monobath composition containing a photographic silver halide developing agent for reducing exposed silver halide to metallic silver and at least 80 grams per liter of solution of a water-soluble thiosulfate, the improvement comprising adding to said monobath from about 0.001 to about 1.0 gram per liter of solution of a heterocyclic mercaptan selected from the class consisting of 1-phenyl-5-mercaptotetrazole, 2-mercapto-5-o-hydroxyphenyl-1,3,4-thiadiazole, 2-mercapto-5-o-tolyl-1,3,4-oxadiazole, 2-mercapto-5-phenyl-1,3,4-oxadiazole, 2-mercapto-5-p-nitrophenyl-1,3,4-oxadiazole, 2-

mercapto-5-cyclohexyl-1,3,4-thiadiazole, and 2-mercapto-5-m-nitrophenyl-1,3,4-oxadiazole.

18. In a process according to claim 17, the improvement comprising adding a small quantity of a water-soluble hydroxyalkylamine to said monobath.

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